

SULFUR DIOXIDE SORPTION REACTIVITY OF HYDRATED LIME: EFFECT OF HYDRATION METHOD

D. L. Moran, M. Rostam-Abadi, R. D. Harvey, and R. R. Frost
Illinois State Geological Survey, Champaign, Illinois 61820

and

G. C. Sresty
Illinois Institute of Technology Research Institute

INTRODUCTION

The Furnace Sorbent Injection (FSI) process is a relatively low capital cost technology for control of SO_2 emissions produced during combustion of high sulfur coal. A major factor in the total cost of the FSI concept is the effective utilization of the sorbent. In pilot plant tests performed by previous investigators, calcium utilization efficiencies (at Ca/S feed ratio of 2:1) ranged from 15 to 20% for limestone, 25 to 30% for dolomitic limestone, 20 to 30% for hydrated lime, and 35 to 40% for pressure-hydrated dolomitic lime (1,2,3,4). The low calcium utilizations observed in these and many other studies have motivated researchers to develop methods of producing more reactive calcium-based sorbents with the goal of reducing SO_2 removal costs.

The hydration method has received considerable attention in recent years because it appears to be the least expensive method of producing fine (<10 micrometer) lime particles with high surface area. Particles of this size range are more reactive than larger particles because they lack significant resistance to pore diffusion. Recent hydration studies have focused on developing sorbents with higher surface areas than those of commercial hydrates. In laboratory-scale hydrators, under controlled processing conditions, hydroxides having surface areas ranging from 42 to 50 m^2/g (2 to 3 times greater than those of commercial hydrates) have been produced (4,5,6,7). Materials with surface areas up to 45 m^2/g have been produced by hydration with methanol-water solutions (7,8).

The objective of this investigation was to produce hydrated lime with high surface area. Three hydration methods were studied: 1) lime was hydrated with water or alcohol-water solutions, 2) lime was reacted with water at pressures and temperatures up to and exceeding supercritical conditions and the hydrated lime produced was ejected to atmospheric conditions, 3) lime was hydrated with steam. Sulfur dioxide sorption capacities were obtained by thermogravimetry and surface areas were determined by the BET (N_2) technique.

EXPERIMENTAL

Materials

Two different limestones were calcined for the experiments (table 1). Both consisted of more than 95% CaCO_3 (calcite). Limestone A is characterized as coarse grained and low specific gravity and limestone B as fine grained and somewhat higher specific gravity.

Calcination

The limestones were calcined in a 2.5-cm I.D. batch fluidized bed reactor constructed from a type 316 stainless steel pipe. Twenty to fifty grams of limestone (100-150 micrometer particles) were heated at a rate of $20^\circ\text{C}/\text{min}$ to 850°C . The sample was held at this temperature for 30 minutes to assure complete conversion of carbonate to lime. Nitrogen was the fluidizing gas flowing at a rate of 1000 cc/min (STP).

Hydration

A 500 ml, three-neck flask was used to hydrate the lime at atmospheric pressure with water or alcohol-water mixtures. Two methods were used: 1) dry hydration (twice stoichiometric water or less) and 2) wet hydration (five times stoichiometric water or more). The hydrate was prepared by adding hydrating solution to one gram of lime while stirring the mixture. The temperature of the mixture increased from ambient to between 50 and 90°C due to the exothermic nature of the hydration reaction. Some of the hydrating solution boiled off during dry hydration runs as a result of localized overheating. The reaction was assumed to be complete after the sample had cooled to room temperature. The hydrated lime product was dried under vacuum and gently crushed for one to two minutes to break up loosely agglomerated particles. Some of the products were filtered and washed with 3 to 25 ml of alcohol prior to vacuum drying. The products were stored in vials under nitrogen to avoid recarbonation.

Pressure-hydrated lime was prepared at the Illinois Institute of Technology Research Institute in a batch reactor constructed of 1.3-cm I.D. stainless steel pipe. The reactor consisted of two sections separated by a metal disk that was designed to rupture at a specific pressure. The upper portion of the reactor (6.4 cm) was charged with one gram of lime and three to four grams of water, capped, and quickly heated using a torch. During the heating period (4 to 5 minutes), the pressure and temperature of the reactor simultaneously increased until the disk ruptured. During this rupturing period (on the order of milliseconds) the reactor pressure dropped to one atmosphere. The pressure-hydrated lime slurry was collected in the lower portion of the reactor (30 cm). The product was vacuum-dried prior to testing for sulfation reactivity.

Lime was hydrated with steam at 200°C for 30 to 60 minutes in a thermogravimetric analyzer system. The partial pressure of steam in the reactor was 0.13 atmospheres. The hydration was assumed to be complete when no further increase in weight was observed. The product was then heated in nitrogen at 20°C/min to 850°C and was tested for sulfation reactivity.

SO₂ reactivity

Reactivity data were obtained by Thermogravimetry (TG) using a Cahn RG balance. The sample holder (1-cm diameter and 0.5-cm height) was constructed of 100 mesh platinum gauze and was suspended from the microbalance by a platinum wire (0.01-cm diameter). The reaction temperature was measured by a Pt/Pt-13% Rh thermocouple located 5 mm below the sample holder. The reactant gas was passed upward through the reactor tube (3.2-cm I.D.). The lower portion of the reactor (10 cm) was filled with 0.64-cm ceramic raschig rings which served as a gas mixing and pre-heating zone and as a gas distributor. The system was interfaced with an IBM-PC to provide automated collection and storage of the microbalance and thermocouple outputs.

In a typical run, sample particles were dispersed in layers of quartz wool located in the sample holder. The sample was heated in nitrogen at a rate of 20°C/min to 850°C. The reaction gas containing 0.5% SO₂, 5% O₂, 20% CO₂, and balance N₂ (which simulated the flue gas from combustion of a high sulfur coal) was introduced to the reactor and the increase in weight due to sulfation and the reaction temperature were recorded at 10 second intervals for 60 minutes. Results of preliminary experiments revealed that sulfation rates were not affected when sample weights of less than 10 mg and gas flow rates between 300 and 900 cc/min (STP) were used. Sample weights of 8 mg and flow rates of 300 cc/min were used in subsequent experiments.

RESULTS AND DISCUSSION

Physical characteristics of hydrates

Hydrated lime products were examined under a light microscope. Dry-hydrated (atmospheric) lime and a commercial pressure-hydrated lime prepared from limestone B consisted of particles which were predominantly less than 10 micrometers in diameter. However, some 10 to 50 micrometer particles were present in the atmospheric hydrate. Reduction in particle size ($mmd=2$ to 4 micrometers) is achieved in commercial pressure hydration processes due to the ejection of the products through an orifice (9). The surface area, BET (N_2), of the pressure-hydrated lime was $17.2 \text{ m}^2/\text{g}$ compared to $34.3 \text{ m}^2/\text{g}$ for the atmospheric product (table 2).

Wet hydration produced agglomerated particles with clusters as large as 0.5 cm. The agglomerates were easily reduced in size by gently crushing with a spatula. However, several large particles were observed in the samples even after crushing. Examination of lime A hydrated with twenty times stoichiometric water followed by vacuum-drying and mild crushing showed that particles were predominantly less than 20 micrometers in diameter, although some as large as 150 micrometers were also present.

Hydration with methanol-water solutions generally produced hydroxides with particles that were finer and more uniform than those prepared with water alone. Few particles greater than 20 microns were observed in these samples. Depending on the amount of methanol used, surface areas ranging from 43 to $70 \text{ m}^2/\text{g}$ were obtained (table 3). Comparable surface areas were obtained for products hydrated with ethanol-water solutions. These values show improvement over surface areas of hydrates prepared in water alone and are three to five times greater than those of commercially available hydrates.

SO₂ reactivity

As described earlier, the hydrated samples were heated in nitrogen to 850°C prior to sulfation. A weight loss of 21-23% was observed between 350 and 500°C due to the dehydration reaction. The theoretical weight loss for the dehydration of pure calcium hydroxide is 24%. The samples lost an additional 1-3% weight between 500 and 700°C . This weight loss was attributed to the calcination of any residual carbonate material in the sample.

The progressive increase in weight during sulfation was attributed to the reaction of the calcined product with oxygen and sulfur dioxide according to:



X-ray diffraction analyses of samples exposed to the reaction gas mixture confirmed that calcium sulfate was the sole product formed. The following relationship was used to calculate the percent conversion (calcium utilization) of the sorbent as a function of reaction time:

$$\text{Percent conversion} = X_t = \frac{W_t - W_0}{Y W_0} \frac{M_{\text{CaO}}}{M_{\text{SO}_3}} \times 100 \quad 2)$$

where: W_t = weight of sorbent at time t
 W_0 = initial weight of sorbent at 850°C
 Y = weight fraction of calcium oxide in sample at 850°C
 M_{CaO} = molecular weight of calcium oxide
 M_{SO_3} = molecular weight of sulfur trioxide

Reactivity curves were obtained by plotting X_t against sulfation time.

Hydration with water

The sorption capacities of hydrates prepared at atmospheric pressure depended on the method of hydration (dry or wet) and the parent limestone (figure 1). The surface areas of the dry and wet hydrates produced from lime A were 37 and 46 m²/g compared to the value of 13 m²/g for the starting lime (100x150 micrometers). The calcium utilizations of these samples were 59, 69 and 37%, respectively. No improvement in utilization was achieved for samples hydrated with five times stoichiometric water or more. Dry and wet hydrates produced from lime B had surface areas which were similar to those obtained for hydrates prepared from lime A (table 2). However, hydrates prepared from lime B had calcium utilizations exceeding 90%.

The results of a recent study showed that calcination conditions, i.e. temperature and sintering time, were not important in producing hydroxides with high surface areas (6). The effect of calcination atmosphere was not investigated in that study. A sample was prepared by calcination of limestone A in one atmosphere carbon dioxide followed by hydration with twenty times stoichiometric water. This treatment increased the utilization of wet hydrate to 78% (vs 69% for hydrate produced from limestone calcined in nitrogen). The sorbent surface area was 33 m²/g, surprisingly lower than that of the hydrate produced from lime prepared in nitrogen atmosphere (46 m²/g).

Sulfation data for the -325 mesh (<45 micrometers) and 100x150 micrometer limes are also shown in figure 1 for comparison. These samples were calcined in the TGA system prior to sulfation. It is interesting to note that although hydrates made from limestone B were more reactive than those made from limestone A, the -325 mesh calcine of the latter (surface area of 20 m²/g) was more reactive than that of the former. Little difference in reactivity was observed for the 100x150 micrometer particles.

Hydration with methanol-water solution

Hydration of lime with alcohol-water solution was tested because a previous study had shown that this method of hydration produced samples with surface areas as high as 50 m²/g (10). Alcohol affects the solubility and interfacial tension of hydrates in water and acts as a dispersing agent, thus minimizing particle agglomeration. The reactivity data for lime B hydrated with a 50% methanol-water solution and washed with ten grams of methanol are shown in figure 1. This sample had a sulfation capacity which was greater than that of the commercially prepared pressure-hydrated lime. A sorption capacity of 100% was observed for this sample as compared to 95% for the commercial hydrate. High calcium utilizations were also observed for samples prepared by hydration of lime A with methanol or ethanol-water solutions (see table 3). This indicates that costs associated with pressure hydration can be eliminated by hydration with methanol-water solution at atmospheric pressure.

Limestone A was subjected to a more extensive study on this method of hydration. The objective was to evaluate the effects of the concentration of alcohol in the hydrating solution and the amount of alcohol used in the post-hydration washing step on the reactivity of the products. The hydration conditions, calcium utilizations and surface areas of the hydrates are summarized in table 3. Reactivity data are shown in figure 2. Increasing the concentration of methanol in the hydrating solution and the amount used in the post-hydration wash resulted in increased calcium utilizations. This is clearly shown in figure 3 where the calcium conversions after 60 minutes are plotted as a function of methanol concentration.

The relationship between the surface area and calcium utilization for the hydrates prepared in methanol-water solution is shown in figure 4. BET (N_2) surface areas of hydrates (prior to dehydration) correlated well with ultimate sorption capacities.

Pressure hydration

The sulfation data for the pressure-hydrated products (Lime A) are shown in figure 5. The calcium conversion of the product prepared at 475 atmospheres and 480°C was 76%. The surface area of this sorbent was 15.4 m^2/g . A conversion of 91% was achieved for the sample prepared at 120 atmospheres and 290°C. The reason for the higher capacity observed for this sample is not known. Although the sulfation capacities of the products prepared under pressure were higher than those of the wet hydrates, their surface areas were lower (see table 2).

Steam hydration

The reactivity of the steam-hydrated lime A is also shown in figure 5. A calcium utilization of 68 % was observed for the hydrated sorbent. This is comparable to the utilization observed for the lime hydrated with water (wet method) at atmospheric pressure. Calcination of limestone under a carbon dioxide atmosphere prior to steam hydration did not influence the reactivity of the sorbent.

CONCLUSIONS

Hydration of lime with alcohol-water solution (ethanol or methanol) at atmospheric pressure produced sorbents with surface areas as high as 75 m^2/g . The hydrates had sulfur dioxide sorption capacities equal to or greater than those of commercially prepared pressure-hydrated limes. Calcium utilization depended on the parent limestone, the concentration of alcohol in the hydrating solution and the amount of alcohol used during the post-hydration step. A linear relationship was obtained between calcium utilization and BET (N_2) surface area. Reactivities of the samples tested showed the following trend:

Ethanol-water hydration = methanol-water hydration > pressure hydration > steam hydration = hydration with water > lime

Finally, it should be noted that the calcium utilizations were obtained at 850°C for sulfation times of 60 minutes. For practical application of results, reactivity data should be evaluated under conditions representative of coal-fired boilers, i.e. high temperature, short residence time.

ACKNOWLEDGEMENTS

We gratefully acknowledge the Illinois Coal Industry Committee and the Center for Research on Sulfur in Coal for their financial support of this project.

REFERENCES

1. Attig, R. C., and Sedor, P., Additive Injection for Sulfur Dioxide Control: EPA report APTD 1176 (NTIS PB 226-761) March, 1970.
2. Beittel, R., Gooch, J. P., Dismukes, E. B., and Muzio, L. J., Studies of Sorbent Calcination and SO_2 -Sorbent Reactions in a Pilot-Scale Furnace. Proceedings: First Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 1, p. 16-1, July, 1985.
3. Payne, R., and Abele, A. R., Evaluation of Low- NO_x Burners for SO_2 Control. Proceedings: First Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 1, p. 21-1, July, 1985.

4. McCarthy, J. M., Chen, S. L., Kramlich, J. C., Seeker, W. R., and Pershing, D. W., Reactivity of Atmospheric and Pressure Hydrated Sorbents for SO₂ Control. Proceedings: 1986 Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1, p. 10-1, December, 1986.
5. Yoon, H., Stouffer, M. R., Rosenhoover, W. A., and Statnick, R. M., Laboratory and Field Development of Coolside SO₂ Abatement Technology. Proceedings of the Second Pittsburg Coal Conference, U. S. DOE, Pittsburgh, PA, p.223, 1985.
6. Borgwardt, R. H., and Bruce, K. R., EPA Study of Hydroxide Reactivity in a Differential Reactor. Proceedings: 1986 Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1, p. 15-1, December, 1986.
7. Gooch, J. P., Dismukes, E.B., Beittel, R., Thompson, J. L., and Rakes, S. L., Sorbent Development and Production Studies. Proceedings: 1986 Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1, p. 11-1, December, 1986.
8. Muzio, L. J., Offen, G. R., Boni, A. A., and Beittel, R., The Effectiveness of Additives for Enhancing SO₂ Removal with Calcium Based Sorbents. Proceedings: 1986 Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1, p. 13-1, December, 1986.
9. Weber, G. F., Schelkoph, G. L., and Ness, H. M., Pilot Scale Studies of Simultaneous Control of SO_x/NO_x Emissions Derived from the Combustion of Low-Rank Coal. Proceedings: 1st Annual Pittsburgh Coal Conference, p.241, Sept, 1984.
10. Staley, H., Micrometrics of Lime, Research Report to National Lime Association, 1946.

Table 1. Characterization of limestones *

Sample ID Location	Geologic unit Grain-size	Spec. grav.	CaO	MgO	CO ₂	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	Na ₂ O
<u>Limestone A</u> Western Ill.	<u>Burlington Ls.</u> Coarse	2.61	53.8	0.3	42.6	0.1	tr ⁺	1.1	0.02
<u>Limestone B</u> Upper Mich.	<u>Fiborn Ls.</u> Fine	2.64	54.3	0.9	43.8	0.2	0.2	0.7	nil

* Analyses in weight percent.

+ trace

Table 2. Summary of sulfation data of hydrates

Limestone	Particle size ^a (mesh)	Calcination atmosphere	Hydration method	Calcium conversion ^b %	Surface area (m ² /g)
B ^c	-100	---	---	95	17.2
A	100x150	N ₂	steam	68	---
A	100x150	N ₂	475 atm	76	15.4
A	100x150	N ₂	120 atm	91	21.4
A	-325	N ₂	none	85	20.7
B	-325	N ₂	none	75	---
B	100x150	N ₂	dry	93	34.3
A	100x150	N ₂	dry	59	37.4
A	100x150	N ₂	wet (20xstoich)	67	47.3
B	100x150	N ₂	wet (20xstoich)	94	49.0
A	100x150	N ₂	none	37	12.9
A	100x150	N ₂	wet (5xstoich)	69	46.1
A	100x150	CO ₂	wet (20xstoich)	78	33.3
A	100x150	CO ₂	steam	68	10.5
B	100x150	N ₂	none	33	---

^aparticle size prior to hydration step

b after 60 minutes

^ccommercial hydrateTable 3. Summary of sulfation data of alcohol-water hydrates^{a,b}

TG No.	Hydration method	Concentration of alcohol in solution weight %	Amount of alcohol wash gm/gm lime	Calcium conversion ^c %	Surface area (m ² /g)
91	dry (2xstoich)	0	0	59	37.4
92	dry (2xstoich)	10	0	67	43.5
98	dry (2xstoich)	50	0	79	64.3
106	wet (5xstoich)	0	0	69	46.1
104	wet (5xstoich)	0	7	79	49.1
105	wet (5xstoich)	30	0	79	44.7
96	wet (5xstoich)	30	3	86	66.4
100	wet (5xstoich)	30	7	93	70.1
95	wet (20xstoich)	0	0	67	47.3
93	wet (15xstoich)	14	10	94	59.4
97	wet (10xstoich)	10	3	78	53.9
89	wet (10xstoich)	50	25	96	63.7
90	wet (10xstoich)	50	25	94	75.3
108	wet (10xstoich)	50	10	100	---

^ahydrates were produced from lime A except TG 108 which was prepared from Lime B^bmethanol was used for alcohol-water hydration tests except for TG 90 ethanol was used^cafter 60 minutes

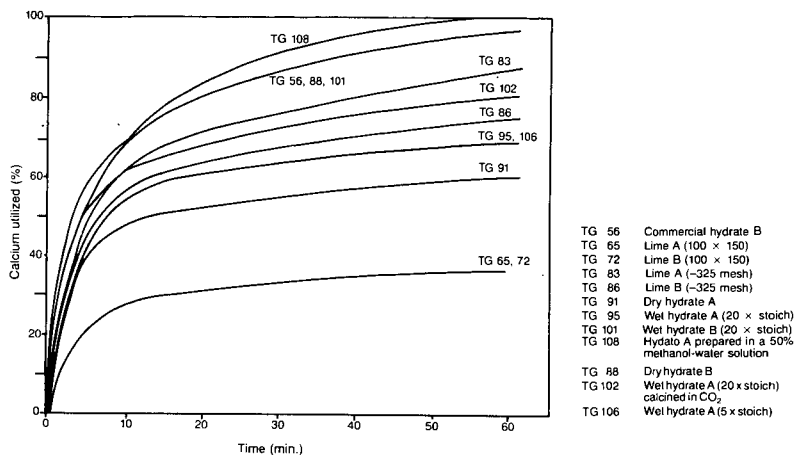


Figure 1. The effects of hydration method, parent limestone, and calcination atmosphere on the reactivity of hydrates.

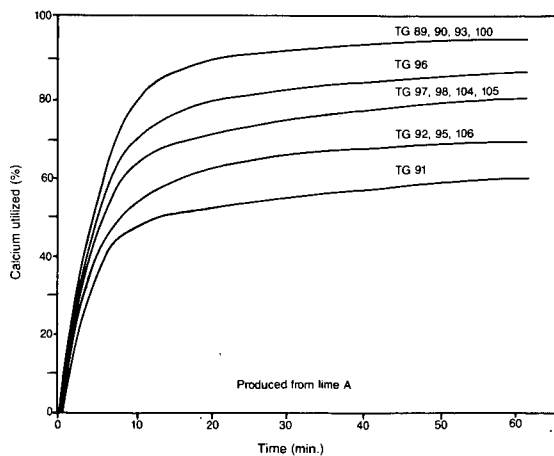


Figure 2. Sulfation reactivities of alcohol-water hydrates.

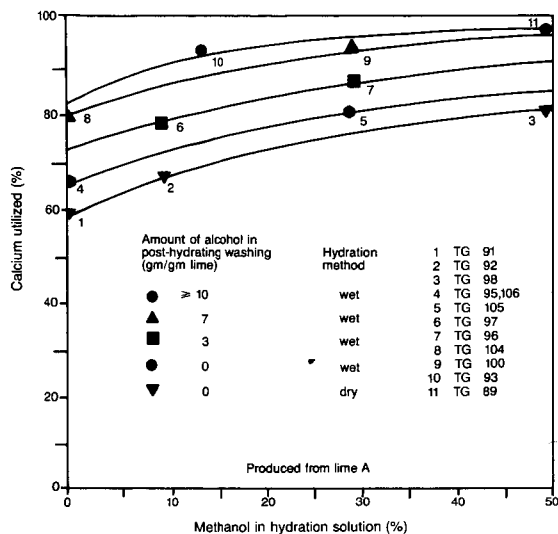


Figure 3. The influence of methanol on hydrated products.

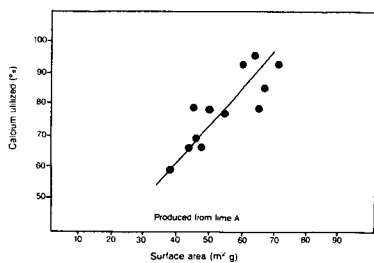


Figure 4. Relationship between calcium utilization and surface area for methanol-water hydrates.

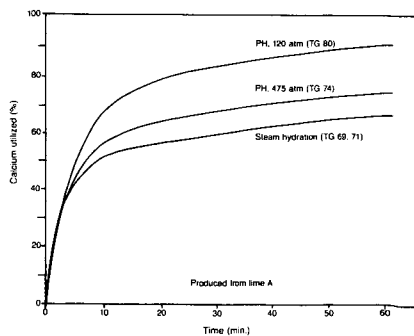


Figure 5. Sulfation reactivities of samples prepared by steam and pressure hydration (PH) methods.